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MARTIN MARIETTA
MANNED SPACE SYSTEMS

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ET Project Reduction of Toxicity in External Tank Coating Systems

Technical Study Annual Report

October 23, 1992

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TECHNICAL STUDY

ANNUAL REPORT

MMC-ET-SE52-3

OCTOBER 23, 1992

REDUCTION OF TOXICITY IN EXTERNAL TANK **COATING SYSTEMS**

Structural Materials

P.L. Hinkeldey, Section Chief Structural Materials

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1.0 **EXECUTIVE SUMMARY**

Potential stringent regulations on products presenting health or environmental hazards require industry to develop low toxicity alternatives to various processing chemicals. This technical study concentrates on evaluating less toxic alternatives for the External Tank (ET) coating systems.

This year's effort was two phased. Due to California and Texas air quality regulations, effective January 1, 1993, emphasis was placed on evaluating epoxy primer systems with lower Volatile Organic Content (VOC) emission levels (i.e., high solids content). The first phase of this study addressed evaluating alternate primer systems to ensure that priming operations by vendors in these states continue. Five separate low VOC primer systems were evaluated through initial screening tests. The alternate materials were evaluated with regard to corrosion resistance, room temperature and cryogenic primer adhesion, and SLA cryoflex adhesion. None of the alternate materials successfully met STM K719 requirements; consequently, no alternative primer systems entered a qualification program. DeSoto Inc. (manufacturer of the current MMS K719 primer) had submitted a new formulation to be tested in FY '93. DeSoto's commitment to develop less toxic alternatives based on the current K719 formulation appears to be the best opportunity to finding an alternative. It was recommended that the newly formulated system submitted by DeSoto continue initial screening tests and, upon passing the SLA cryoflex adhesion test, begin engineering qualification tests.

The strippable process coating, Adcoat 828, otherwise known as "elephant hide", is a material containing the high VOC solvent perchloroethylene, for spray-on applications. California state law. effective January 1, 1993, specifies that perchloroethylene emission levels shall be reduced by 5% per year based on 1990-91 emissions. The second phase of this study addressed alternative forms of strippable processing maskants. Adcoat 828 provides protection for chem-milled hardware against corrosion and contamination from handling. In the past, water-borne strippable coatings have been evaluated at MAF with no success. One water-borne coating developed by Malek, Inc. appears to meet ET requirements and is currently under evaluation for ease of peelability; corrosion protection; compatibility with weld operations: and subsequent primer adhesion after removal. Alternative forms of coating chem-milled panels are under evaluation. One such material, Rapgard™, is a polyolefin plastic film with an adhesive backing. It is applied by hand and eliminates the need for solvents. Initial tests indicate successful results. It was recommended that evaluation of the large-scale feasibility of Rapgard™ continue. FY '93 effort shall be extended to determine if other methods of protecting chem-milled hardware are sufficient for MAF usage.

2.0 <u>INTRODUCTION</u>

Increasing public awareness of the effects hazardous waste disposal has on the environment has led to stricter Environmental Protection Agency (EPA) regulations. Louisiana enacted legislation requires Martin Marietta Manned Space Systems (MMMSS) to implement active programs to reduce hazardous waste disposal either through recapture equipment or through processing changes. This technical study addresses the need for less toxic alternatives for the External Tank (ET) coating systems.

The currently used epoxy primer system contains chromates (an environmental and health hazard), methyl ethyl ketone (a high VOC solvent), and cellosolve acetate (a mutagen and teratogen). The solvent system (MEK and cyclohexanone) for the epoxy primer has a high volatile organic content (VOC) level. This level does not meet Aerospace Coating Primer emission requirements established by the California and Texas state Air Quality Management District regulations. This study addresses qualification of alternate primer systems to allow work by vendors in these states to continue.

The strippable process coating, Adcoat 828, otherwise known as "elephant hide", is a solvent based material containing perchloroethylene. Perchloroethylene is a high VOC solvent and California state law specifies that perchlororethylene emissions shall reduce 5% per year from 1990-'91 levels beginning January, 1993. Adcoat is applied to chem-milled gore panels and domes at vendors in California. Vendors have informed Martin Marietta that due to the new emission regulations, their application of Adcoat will cease by July, 1993. Because of these pending regulations and potential hazards associated with the epoxy primer and processing maskants, active programs to qualify less toxic alternative materials which meet ET service requirements are in place. This report discusses the results and findings of these efforts.

3.0 **OBJECTIVES** 3.1 The first objective of this study was to identify and evaluate alternative materials for the epoxy primer system. 3.2 The second objective of this study was to identify and evaluate alternative processing maskants. **CONCLUSIONS** 4.0 4.1 The new high solids primer, DeSoto 533K009, was the only alternative, low VOC material that showed any promise as a replacement for the current epoxy primer system. 4.2 Two alternative processing maskants, water-borne Malek MBP-100 and Rapgard™ protective film, show promise and remain in evaluation. 5.0 RECOMMENDATIONS 5.1 It is recommended that the newly formulated DeSoto 533K009 high solids primer continue initial screening tests. 5.2 It is recommended that upon passing the SLA cryoflex screening test, DeSoto 533K009 primer begin engineering qualification tests. 5.3 It is recommended that water-borne Malek MBP-100 continue testing as an alternative strippable coating.

It is recommended that the large-scale feasibility of Rapgard™

protective film continue evaluation.

5.4

6.0 <u>DISCUSSION OF RESULTS</u>

Due to the California state AQMD regulations, effective January 1, 1993, emphasis was placed on evaluating alternative epoxy primer systems that have lower VOC emission levels. The current epoxy primer system has a VOC level of 650g/l. California state regulations prohibit the use of Aerospace Coating Primers with VOC levels above 350 g/l. Martin Marietta was recently informed that the Texas state Air Control Board will enact regulations effective January 1, 1993 that will prohibit the use of paints (all types included) exceeding VOC levels of 6.7 lb/gal of solids. For the 60% solids material MMS K719, this converts to ~482 g/l.

With these regulations in mind, this program evaluated low VOC epoxy primer systems. These systems were characterized as high solids primers which eliminate the solvent reducer. Typically, solvent reduced materials have a working pot life of thirty hours or more. The high solids primer system's have pot life times well below current production time schedules. In coordination with Production Operations it was felt that adjustments in manufacturing time schedules could be made in order to accomodate the working pot life of a low VOC material.

Five separate low VOC primer systems were evaluated through initial screening tests (reference Appendix A): DeSoto 533K003, Sunbelt 33-019, Dexter 26F30100, 3M Scotchweld EC3982, and Scotchweld EC3983. It should be noted that the high solids primers were 2-part systems rather than the current 3-part system DeSoto 515x346 (MMS K719). The alternate materials were evaluated in comparison to the current MMS K719 epoxy primer with regard to corrosion resistance, room temperature and cryogenic primer adhesion, and SLA cryoflex adhesion. The SLA is a very dense ablator material which places large stresses on the primer-to-substrate interface during cryoflex testing. A primer must have relatively high adhesion to meet the SLA cryoflex requirement.

The only material to pass the screening test requirements of STM K719 was the DeSto 533K003. Both 3M Scotchweld products failed the corrosion test after exposure at 120°F/100% RH and 5% salt spray for 1000 hours. The Sunbelt 33019 and Dexter 26F3011 products did not pass adhesion performance, failing tensile adhesion requirements of STM K719. Due to its success through the initial screening tests DeSoto 533k003 high solids primer was to be evaluated per SLA cryoflex testing. However, prior to performing these tests it was observed that the 533k003 system had a shelf life concern. After four months the DeSoto 533k003 base had coagulated; the solids settling within the system. DeSoto became aware of this settling problem and modified the 533k003 formulation. DeSoto submitted a new high solids formulation (533k009) to be tested in FY '93. Due to the outcome of the screening tests no alternative primer systems entered a qualification program.

DeSoto is a California based manufacturer of paints and was aware of the state AQMD regulations concerning their primer systems. DeSoto's commitment to develop less toxic alternatives based on the current K719 formulation appears to be the best opportunity to finding an alternative.

As part of the effort to reduce the toxicity of ET coating systems, alternative forms of strippable coatings have been evaluated. The current strippable coating, Adcoat 828, contains perchloroethylene as a solvent for spray-on applications. The strippable coating is applied to chem-milled surfaces by vendors after chem-milling and subsequent cleaning operations. Adcoat provides protection against corrosion and contamination from handling, and is removed by hand prior to tank level cleaning.

In the past, water-borne strippable coatings have been evaluated at MAF, with no success. One water-borne processing maskant has been developed by Malek, Inc. which appears to meet ET requirements and California VOC regulations. The maskant, Malek MBP-100, was applied to chem-milled panels at the vendor and sheduled for tests at MAF (reference Appendix B). The coating shall undergo evaluation for ease of peelability, corrosion protection, compatibility with weld operations, and subsequent primer adhesion after removal. Due to problems with chem-milling operations at Malek, testing of the water-borne coating was delayed.

An alternative form of coating chem-milled panels is currently in test. Since spray-on application results in using a solvent, hand applied material are the possible answer to this environmental issue. DuPont, in a joint venture with Kansai Inc., has developed RapgardTM, a temporary protective film for transportation and storage of automobiles overseas. RapgardTM is a polyolefin thermoplastic film with an adhesive backing. The film is in sheet form and applied by hand; therefore, eliminating the need for solvents. Initial tests (reference Appendix C) of the RapgardTM film appear to give positive results. Testing will continue in order to determine the large scale feasability of using a protective film in replacement of the solvent-based Adcoat 828. Efforts shall be extended to determine if other methods of protecting chem-milled hardware are sufficient for MAF usage.

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Appendix A:

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Materials Engineering

Test Plan

ETTP-409

Evaluation of Alternate Primers for ET Use

A. C. Lander, Sr. Engineer Structural Materials

Approved by:

Structural Materials

P. L. Hinkeldey, Section Chief

Structural Materials

1.0 INTRODUCTION

Due to Environmental Protection Agency (EPA) regulations, there has been an ongoing evaluation of alternate primer systems. The present epoxy primer system is a sole source material with a high volatile organic content (VOC). In addition, it contains chromates (a suspect carcinogen), methyl ethyl ketone (MEK - a flammable solvent), and cellosolve acetate (a suspect mutagen and teratogen). More stringent regulations of these compounds and of the total VOC are expected in the near future. Unless a waiver is obtained, use of the present primer will be restricted.

This test plan will evaluate alternate primer for cryogenic adhesion, corrosion resistance and primer adhesion. SLA cryoflex testing is included since two earlier tested materials passed all testing except for this test.

2.0 OBJECTIVE

2.1 The objective of this test plan is to evaluate alternate primer materials for use on the External Tank (ET).

3.0 MATERIALS

- 3.1 100 0.040" x 1.0" 4.0" 2219-T87 Aluminum panels precleaned per STP 5006; MII.
- 3.2 50 0.125" x 3.0" x 10.0" 2219-T87 Aluminum panels precleaned per STP 5006; MII.
- 3.3 50 0.125" x 4.0" x 6.0" 2219-T87 Aluminum panels precleaned per STP 5006; MII.
- 3.4 10 0.125" x 24.0" x 24.0" 2219-T87 Aluminum panels precleaned per STP 5006; MII.
- 3.5 Alternate primer materials submitted by vendors.

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4.0 TEST PROCEDURE

The following tests shall be performed on each sample of primer submitted for testing plus the DeSoto MMSK719 epoxy primer.

- 4.1 Cryogenic finger flexure
 - (A) Spray ten 1" x 4" panels for each primer received.
 - (B) Cool five finger panels and the pentagon mandrel bend fixture to -320°F. Bend each panel over the 1" mandrel. Record any change in primer adhesion on appearance. Continue to bend cooled specimens over the other mandrels, proceeding from largest to smallest. Record results for each primer at each size mandrel. Discontinue testing when primer fails (i.e., cracks, loses adhesion).
 - (C) Repeat Step (B) at -423°F.
- 4.2 Salt Fog Resistance
 - (A) Spray five 0.125" x 4.0" x 6.0" panels for each primer received.
 - (B) Expose panels to a five percent salt fog solution per ASTM B117 for a minimum of 1000 hours. After 1000 hours exposure, examine panels for corrosion or any changes in the primer. If there are no failures, place panels back in the salt fog chamber and examine panels every 168 hours. When the primer fails, strip the panels and examine for corrosion. Record results for all primers.
- 4.3 Primer Adhesion
 - (A) Spray five 0.125" x 3.0" x 10" panels with each primer received.
 - (B) Perform two wet adhesion tape tests per panel. Record results.
 - (C) Perform three Elcometer adhesion tests on each panel. Record results and mode of failure.

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4.4 SLA Cryoflex

- (A) Spray one 0.125" x 24.0" x 24.0" panels with each primer received.
- (B) Bond a SLA-561m panel to the primed panels and fabricate cryoflex and density specimens.
- (C) Test SLA cryoflex specimens per EQTP 1001 (latest revision) @ -423°F, ∞ radius, pull to tape failure (or 70 ksi).

5.0 RESPONSIBILITIES

- 5.1 Dept. 3581 will be responsible for all testing, coordination of priming operations, application of ablator, and recording of data.
- 5.2 Dept. 3573 will be responsible for analysis of data and writing of final engineering evaluation.

6.0 BUDGET

6.1 All work performed on this test plan shall be charged to 453607-81500-31710-E1727.





Structural Materials

Test Plan

ETTP-415

Evaluation of Malek MBP-100 Waterborne Chemical Processing Maskant

March, 1992

Prepared by:

Approved by:

J. F. Knoll, Sr. Group Engineer Structural Materials

P. L. Hinkeldey, Section Chief

Structural Materials

1.0 INTRODUCTION

As part of the effort to reduce the toxicity of ET Coating Systems, manufacturers of chemical processing maskants have been contacted for available alternatives. Malek, Inc., a San Diego based company, has developed a waterborne chemical processing maskant which appears to meet ET requirements and California VOC regulations. Malek, Inc. has offered to chem mill and coat panels with the chemical processing maskant. The panels will be sent back to MAF where testing will be performed. The coating will be evaluated for ease of peelability, corrosion protection, compatibility with weld operations, and subsequent primer adhesion.

2.0 OBJECTIVES

- 2.1. The first objective is to determine if the Malek MBP-100 chemical processing maskant meets present ET requirements for corrosion protection and peelability.
- 2.2 The second objective is to evaluate primer adhesion (via wet adhesion tape test Patti Jr., and cryoflex specimens) to verify that no additional processing must be implemented prior to priming.

3.0 MATERIALS

- 3.1 13 24" x 24" x 0.125" 2219-T87 Al panels
- 3.2 DeSoto STM K719 primer
- 3.3 2 25" x 25" SLA 561m panels

4.0 <u>TEST_PROCEDURE</u>

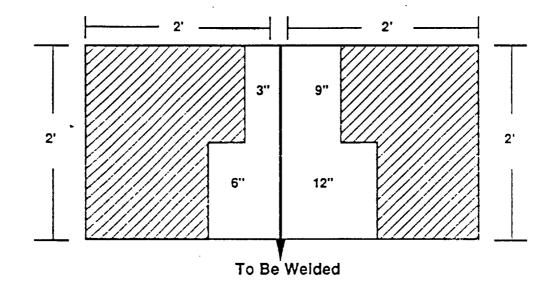
4.1 Wrap and ship panels from 3.1 to:

Mark Jaffari c/o Caspian, Inc 4951 Ruffin Road San Diego, CA 92123

619-279-3110

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- 4.2 After panels are coated, they are to be shipped back to MAF for testing.
- 4.3 The following tests are to be performed on the coated panels:
 - 4.3.1 Two of the 24" x 24" panels are to be welded together to make one 24" x 48" panel. The coating is to be pulled away from the edge prior to welding in increments of 3", 6", 9", and 12" (one foot length for each increment). See diagram below:



- (A) Submit panels to AMT for weld operations. Note any anomalies during welding which could have resulted from residual left by the coating.
- (B) After panels are welded, remove coating from panels. Note difficulties in removing the coating which may have resulted from heat due to weld operations. Record how far the coatings must be removed from the welded edge so as not to be affected by weld operations.
- 4.3.2 A. Strip three 24" x 24" panels by peel test. Record results.
 - B. Strip one 24" x 24" panel marked ambient and one 24" x 24" panel marked 90°F by peel test. Record results.

- 4.3.3 The remaining panels which have not been stripped are to be tested as follows:
 - (A) Place one 24" x 24" panel in a salt spray chamber per ASTM B117 for 168 hours. Record results.
 - (B) Place one 24" x 24" panel in a weatheremeter per Federal Standard 141, Method 6152. Inspect coating for pinholes and uniformity of appearance at 200 hours and 1500 hours. Inspect panel for corrosion. Record results.
 - (C) Flush sections of one 24" x 24" panel from each vendor condition (ambient, 90°F, and non-marked) with MEK, trichloroethylene, Freon and isopropyl alcohol to determine solvent resistance. Record results.
 - (D) Place one 24" x 24" panel in storage for six months. Strip the panel by peel test. Record results. Inspect panel for corrosion.
- 4.4 After removing the strippable coating from panels in section 4.3.1 and 4.3.2A, prepare the panels as follows:
 - 4.4.1 Clean the stripped panels per STP 5006; MI (do not vapor degrease).
 - 4.4.2 Prime the panels per STP 3004; Type 1.
- 4.5 The above panels are to be tested as outlined below:
 - 4.5.1 Wet adhesion tape test test the 2' x 4' welded panel and one 24" x 24" panel randomly over the entire surface. Record results.
 - 4.5.2 PATTI adhesion tests test the above panels randomly over the entire surface. Record results.
 - 4.5.3 The two remaining 24" x 24" panels are for cryogenic testing. Submit to TPS for application of foam and specimen preparation. Consult Materials Engineering for test parameters and TPS Job Order. Record results.

5.0 RESPONSIBILITIES

5.1 Dept. 4351 Technology Operations will be responsible for welding, coordinating precaration of panels, testing of panels and issuing laboratory report.

5.2 Materials Engineering will be responsible for assisting in testing and writing the final report.

6.0 BUDGET

6.1 All work done on this test plan is to be charged to 453607-81500-31710-E1727.

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STRUCTURAL MATERIALS TEST PLAN

ETTP - 427

Evaluation of Rapgard™ Protective Film as a Processing Maskant

September, 1992

Prepared by:

C.G. Meringer, Engineer Structural Materials

Approved by:

A. Daech, Staff Engineer Structural Materials

P.L. Hinkeldey, Section Chief Structural Materials

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1.0 INTRODUCTION

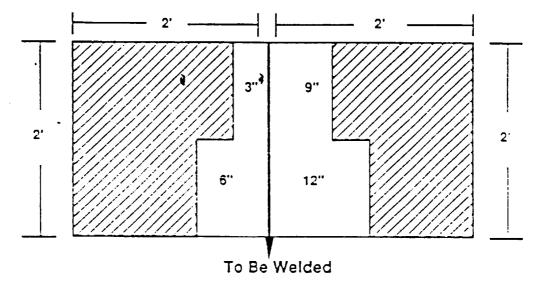
As part of the effort to reduce toxicity of External Tank coating systems, alternative forms of processing maskants are being evaluated. DuPont - Kansai, in a joint venture, have developed RapgardTM, a temporary protective film for transportation and storage of automotive finishes. RapgardTM is a polyolefin thermoplastic film with a polyolefin adhesive backing. The film is applied by hand in sheet form; therefore, eliminating the need for solvents used in applying current processing maskants. California VOC regulations limit the use of solvent based maskants. RapgardTM will be applied to aluminum panels and evaluated for ease of peelability, corrosion protection, compatibility with solvents, and subsequent primer adhesion.

2.0 OBJECTIVES

- 2.1 To determine if Rapgard™ meets present ET requirements for corrosion protection and peelability.
- 2.2 To evaluate primer adhesion to verify that no additional processing must be implemented prior to priming operations.

3.0 TEST PROCEDURE

- 3.1 Preclean per STP 5006, Method II 24" x 24" x 0.125" 2219-T87 aluminum panels.
- 3.2 Apply Rapgard™ protective film over two of the 24" x 24" panels. The panels are to be welded together to make one 24" x 48" panel. The film is to be pulled away from the edges prior to welding in increments of 3", 6", 9", and 12" (one foot length for each increment). See diagram below:



- 3.2.1 Submit panels to AMT for weld operations. Note any anomolies during welding which could have resulted from residual left by the coating.
- 3.2.2 After panels are welded, remove film from the panels. Note any difficulties in removing the film which may have resulted from heat due to weld operations. Record how far the film must be removed from the welded edge so as not to be affected by weld operations.
- 3.3 Apply Rapgard™ film to two 24" x 24" panels. Remove film by peeling by hand. Record any difficulties (stretching, tearing, etc.) in removing film.
- 3.4 Apply Rapgard™ to two 24" x 24" panels, heat to 90° F in an oven, remove panel and perform peel test. Record results.

- 3.5 Apply Rapgard™ to one 24" x 24" panel allowing for at least 3 air bubbles one inch in diameter in the film. Place in a salt spray chamber per ASTM B117 for 168 hours, remove film after drying. Record results.
- 3.6 Apply Rapgard™ to one 24" x 24" panel allowing for at least 3 air bubbles one inch in diameter in the film. Place in a weatherometer per Federal Standard 141, Method 6152. Inspect film for appearance at 200 and 1500 hours. Remove panel from weatherometer, remove film, inspect for corrosion. Record results.
- 3.7 Apply Rapgard™ to one 24" x 24" panel allowing for at least 3 air bubbles one inch in diameter in the film. Flush sections of the panel with MEK, trichloroethylene, Freon TMC, and isopropyl alcohol to determine solvent resistance. Record results.
- 3.8 Apply Rapgard™ to one 24" x 24" panel allowing for at least 3 air bubbles one inch in diameter in the film. Place panel in ambient storage for 6 months. Remove the film, record any difficulties in removing the film, inspect panel for corrosion, Record results.
- 3.9 The 4 panels from 3.3 and 3.4 are to be cleaned per STP 5006, Method I (do not vapor degrease). Prime the panels per STP 3004, Type 1.
- 3.10 One panel from each of 3.3 and 3.4 primed panels are to be undergo the following tests:
 - A) wet adhesion tape test randomly over entire surface, perform 6-8 tests per panel.
 - B) PATTI Jr. adhesion tests randomly over entire surface, perform 6-8 tests per panel.
- 3.11 The two remaining panels from 3.9 are for cryogenic testing. Submit to TPS for application of foam and specimen preparation. Consult engineer for TPS Job Order.

4.0 **RESPONSIBILITIES**

- 4.1 Dept. 4153 shall coordinate testing and evaluate results.
- 4.2 Dept. 4351 shall prepare test panels, perform welding operations, perform tests, and record results.

5.0 BUDGET

All work performed under this test plan shall be charged to 453607-81500-31710-E1727.

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